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NO DRAWINGS

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COMPLETE SPECIFICATION

Liquid Phase Oxidation of Isobutane

We, ATLANTIO RICHFIELD COMPANY, a Corporation organized under the laws of the State of Pennsylvania, United States of America, of 260 South Broad Street, Philadelphia 1, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for increasing the reaction rate in the liquid phase oxidation of isobutane with molecular oxygen.

The liquid phase oxidation of isobutane with molecular oxygen produces two main products, one being tertiary butyl hydroperoxide, and the other being tertiary butyl alcohol. Tertiary butyl hydroperoxide is useful as a starting and intermediate material in the production of valuable chemical derivatives. A particularly important use of this kind is in the oxidation of olefins to their corresponding epoxides in the presence of a heavy metal containing catalyst such as molybdenum-, vanadium-, or tungsten-containing catalyst. Tertiary butyl alcohol is valuable as an octane improver in gasoline.

The oxidation reaction is carried out at temperatures in the range of from 200°F. to about 300°F. under pressures of 300 psig and higher, for example, in the range of from about 400 to 700 psig. The reaction is also preferably carried out in the absence of catalysts, particularly in the absence of metal ions. The presence of a catalyst tends to shift the equilibrium toward the production of increased amounts of alcohol. By proper choice of reaction conditions within these ranges, conversions of isobutane to the desired tertiary butyl hydroperoxide and tertiary butyl alcohol will range between 30 per cent and 70 per cent or higher with hydroperoxide content in the products ranging up to 70 per cent.

The isobutane ordinarily employed in refineries, for example in the production of alkylate for gasoline, contains about 5 per cent normal butane and propane as impurities. In many instances, the amount of these impurities may range as high as 10 to 15 percent. Although it would be expected that as the amount of these impurities increases, the reaction rate (the amount of isobutane converted to products per unit of time) decreases by the simple dilution effect of these impurities, it has been found quite unexpectedly that these impurities exert a much higher decrease in reaction rate than would be predicted by the dilution effect.

According to the present invention there is provided a process for the liquid phase oxidation of isobutane with molecular oxygen at elevated temperatures and pressures in which the charge stream contains at least 97% by weight isobutane and less than 3% of normal butane and propane.

It has been found in accordance with this invention that ordinary commercial grade isobutane cannot be employed in liquid phase oxidation reaction without also obtaining lower reaction rates. In order to increase the reaction rate above that obtainable with commercial grade isobutane, it is necessary that the normal butane content or propane content, or normal butane-propane content be less than about 3 per cent by weight in the isobutane charge stream with the isobutane content of the stream being at least 97 per cent by weight or higher (both percentages being based on the total weight of the stream). Preferably, the content of these impurities should

be less than about 2 per cent by weight with the isobutane content being 98 per cent by weight or more based on the total weight of the stream.

The following examples will serve to illustrate the invention in greater detail.

EXAMPLE I

An isobutane stream consisting of 89.8 weight per cent isobutane and 10.2 weight per cent normal butane was charged to a 24,000 ml capacity stainless steel oxidizer utilizing a small excess of oxygen as the oxidation medium. The reaction was carried out at 290°F. under a pressure of 520 psig with a charge rate of 3000 ml of the isobutane stream per hour. There was obtained a decrease in reaction rate of 27 per cent as compared with the reaction rate obtained when 99.9 per cent purity isobutane was employed under these same reaction conditions. The decrease in reaction which would be expected by the dilution effect alone would be only 10 per cent, assuming zero reactivity for the n-butane. The n-butane, however, has a specific rate of oxidation and therefore the decrease in reaction rate because of the dilution effect is considerably less than 10 per cent. Accordingly, it is seen that normal butane as an impurity has an unexpectedly high effect for decreasing reaction rate.

EXAMPLE II

Another run was carried out utilizing an isobutane stream containing 90.1 weight per cent isobutane and 9.9 weight per cent propane. Thus run was carried out with a charge rate of 2400 ml of the isobutane stream per hour at 290°F. under 550 psig pressure. There was obtained a decrease in reaction rate of 26 per cent as compared with the reaction rate for 99.9 per cent purity isobutane, showing that propane has approximately the same effect for decreasing reaction rate as the normal butane.

EXAMPLE III

Two additional runs were carried out under reaction conditions similar to those set forth in Example I and II. The first run utilized an isobutane stream containing 97 weight per cent isobutane and 3 weight per cent of a mixture of normal butane and propane. It was found that the reaction rate decreased about 5 per cent as compared with the reaction rate for that found in the second run which utilized an isobutane stream containing about 99 weight per cent isobutane and 1 weight per cent normal butane and propane. In the second run the reaction rate was approximately 2 per cent lower than obtained with isobutane of 99.9 per cent purity.

Since for commercial operation, it is desirable to employ a reaction rate which is as high as possible and which in general, is not less than about 10 per cent below the reaction rate which is obtainable with the pure isobutane, it will be seen from the runs set forth in the examples that the isobutane stream should contain less than about 3 per cent by weight of normal butane or propane or mixtures thereof with the isobutane content of the isobutane stream being at least 97 weight per cent of the total stream. Preferably, however, the content of these impurities in the isobutane stream should be less than about 2 per cent by weight based on the weight of the entire stream, with the isobutane content being about 98 weight per cent.

WHAT WE CLAIM IS:—

1. A process for the liquid phase oxidation of isobutane with molecular oxygen at elevated temperatures and pressures in which the charge stream contains at least 97% by weight isobutane and less than 3% of normal butane and propane.

2. A process according to claim 1, in which the content of isobutane is at least 98%.

3. A process for the liquid phase oxidation of isobutane according to claim 1 and substantially as hereinbefore described in the Examples.

4. Oxidation products of isobutane when produced by a process according to any one of claims 1 to 3.

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